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Continuous Hydrothermal Co-liquefaction of Aspen Wood and Glycerol with Water Phase Recirculation

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Abstract

Hydrothermal liquefaction is a promising technology for the conversion of a wide range of bio-feedstock into a biocrude; a mixture of chemical compounds that holds the potential for a renewable production of chemicals and fuels. Most research in hydrothermal liquefaction is performed in batch type reactors, although a continuous and energy-efficient operation is paramount for such process to be feasible. In this work an experimental campaign in a continuous bench scale unit is presented. The campaign is based on glycerol-assisted hydrothermal liquefaction of aspen wood carried out with the presence of a homogeneous catalyst at supercritical water conditions, 400 °C and 300 bar. Furthermore, in the experimental campaign a water phase recirculation step is incorporated to evaluate the technical feasibility of such procedure. In total, four batches of approximately 100 kg of feed each were processed successfully at steady state conditions without any observation of system malfunctioning. The biocrude obtained was characterized using several analytical methods to evaluate the feasibility of the process and the quality of the product. Results showed that a high quality biocrude was obtained having a higher heating value of 34.3 MJ/kg. The volatile fraction of the biocrude consisted mostly of compounds having number of carbon atoms in the C₆-C₁₂ range similar to gasoline. In terms of process feasibility, it was revealed that total organic carbon (TOC) and ash significantly accumulated in the water phase when such is recirculated for the proceeding batch. After four batches the TOC and the ash mass fraction of the water phase were 136.2 [g/L] and 12.6 [%], respectively. Water phase recirculation showed a slight increase in the biocrude quality in terms on an effective hydrogen-to-carbon ratio, but it showed no effects on the product gas composition or the pH of the water phase. The successful operation demonstrated the technical feasibility of a continuous production of high quality biocrude.

Keywords: Biofuel, Continuous processing, Biocrude, Biomass, Hydrothermal liquefaction, Sustainability

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1. Introduction

Hydrothermal conversion of biomass in hot-compressed water is a viable, scalable, and energy-efficient thermo-chemical route for converting biomass into synthetic solid, liquid, or gaseous fuels and chemicals. At near and supercritical water conditions, biomass fragments into a bulk liquid phase, better known as biocrude. It consists of low molecular weight and deoxygenated chemical species compared to the original biomass macromolecules. The biocrude may be further processed into platform chemicals or infrastructure-compatible fuels. Hydrothermal conversion of biomass has been widely studied experimentally, mostly in batch reactors and less so in continuous systems, and has been reviewed in the many process aspects, such as near-critical water synthesis properties [1, 2], the effects of various process conditions [3], effects of biomass composition [4–7], process developments [8–10], and upgrading of the biocrude [11–13].

Although the vast majority of research is carried out in batch reactors, development of continuous operation and technology upscaling of near-critical water technologies has been ongoing since the mid-seventies - but has not yet reached commercialization [9]. The continuous process was first demonstrated at a bench scale system at the Pittsburgh Energy Research Center (PERC) which was later scaled to the Albany plant, Oregon [14]. The production facility utilized a recycle concept in which wood (Douglas fir) was slurried in recycled process water and initially in anthracene oil and eventually in recycled biocrude as it became available. The following three aspects of the process were identified as critical: 1) the energy intensive pre-drying and grinding step required for wood flour preparation, 2) wood-biocrude-water slurries could not be fed at concentrations greater than 10 % without causing system plugging, 3) high recycle ratios of biocrude (up to 19:1) required excessive heat [15]. Many process improvements have since been done, and it is believed that the critical aspects can be overcome or greatly reduced to an extent for the process to become feasible. One aspect of the process optimization is to maximize the biocrude whilst decreasing the amount of solid byproducts. During liquefaction, reactive biomass fragments rearrange to biocrude compounds through condensation, cyclization, and re-polymerization, and for prolonged process severity a solid fraction insoluble in most solvents is formed, which is generally termed char.

In a lignocellulosic context, char formation results primarily from two counteracting mechanisms; 1) dehydration reactions of free sugars favored at intermediate temperatures, high feed concentrations [16], and acidic conditions [17], and 2) radical formation during lignin degradation leading to retrogressive char formation [18]. Char formation from carbohydrates can be suppressed by applying high heating rates to reach high reaction temperatures, preferably above supercritical conditions, and alkaline conditions [16, 19, 20]. Lignin radical formation purely a thermal effect, hence supercritical conditions tends to enhance lignin char formation [21]. Means of overcoming these counteracting thermal effects includes the addition of a reducing agent such hydrogen or carbon monoxide, or by the addition of a stabilizing co-solvent acting as a radical scavenger through hydrogen donation. Alcohols may undergo thermal scission causing hydrogen abstraction in the form of $\cdot\text{H}$, $\cdot\text{OH}$, or $\cdot\text{CH}_2\text{OH}$ radicals, amenable to cap lignin radicals and hence preventing lignin repolymerization [22–24]. Low molecular weight co-solvents such as phenol [25], propanol [26], ethanol [27, 28], methanol [29], and glycerol [30, 31] have been applied, and are preferable in order to obtain

low molecular weight product compounds, when transport fuel precursors are targeted.

Among co-solvents, glycerol is of particular interest since it is already produced in large quantities. Today, glycerol is mainly a refined bio-based by-product from biodiesel production, and its market value has been declining since the market entry of biodiesel production, making it economically interesting. Xiu et al. investigated in batch the potential of utilizing crude glycerol, the unrefined by-product, as a co-substrate in hydrothermal processing of swine manure. It was found that crude glycerol enhanced both the yield and the quality of the biocrude based on the elemental composition [32–37]. In the same studies it was attempted to understand the conversion chemistry involved through model studies using pure glycerol, methanol, and fatty acids as model co-substrates, but the reaction mechanisms of the different organic compounds in the crude glycerol on the biocrude production were not fully established. Moreover, in house, but yet unpublished, model studies in batch reactors have shown that by hydrothermally liquefying aspen wood in the presence of glycerol or crude glycerol, char formation can be significantly reduced whilst maintaining a high yield of high quality biocrude [38].

The objective and novelty of the present study is to investigate and demonstrate continuous co-liquefaction at bench scale conditions of aspen wood and glycerol as a co-solvent as a viable route to process lignocellulose at high organic concentrations in the feed. The technical feasibility of process water phase recirculation is incorporated to evaluate benefits and eventual complications of such procedure. The process is evaluated based on system performance, recirculation effects on phase characteristics, and a product assessment to examine the quality of the obtained biocrude.

2. Materials and Methods

2.1. Materials

Supercritical co-liquefaction of aspen wood and glycerol was demonstrated in the continuous bench scale reactor unit (CBS1) at the Department of Energy Technology, Aalborg University. In total, four batches of approximately 100 kg of feed each were processed, all prepared from the same recipe. Table 1 shows the properties of the aspen wood. Glycerol (99.5 %), potassium carbonate (K_2CO_3), and carboxymethyl cellulose (CMC) were purchased from Brenntag Nordic A/S.

2.2. Process feed composition

Table 2 shows the feed composition used in the experimental campaign. Aspen wood and glycerol were mixed in nearly 50/50 ratios in recycled water phase together with K_2CO_3 and CMC. In the absence of product water phase, the feed for Batch #1 was prepared using distilled water.

2.3. Description of the Continuous Bench-Scale Unit (CBS1)

A process flow diagram (PFD) of the CBS1 is presented in Figure 1. Pretreatment and feed slurry preparation is done in a stand-alone mixer, where aspen wood, glycerol, water phase and catalyst are mixed. Steady state conditions at the preset operating conditions are reached by circulating hot-compressed water (HCW) through the plant. Once reached, the water is replaced by a batch of the prepared feed and continuous biocrude production

Table 1: ^aUltimate analysis was carried out in a Perkin Elmer 2400 Series II CHNS/O system. ^bFibre composition was determined by the Van Soest method in a FOSS Fibertec M6 unit. ^cAsh content measured by heating a sample to 850 °C and held isothermally for 2 hours. daf = dry, ash-free. N.D. = Not Determined

Elemental and ^a ultimate mass analyses (% , daf.)	
C	50.39 (± 0.86)
H	6.19 (± 0.08)
N	0.19 (± 0.02)
S	N.D.
O (by difference)	43.23 (± 0.08)
^b Fibre mass composition (% , db.)	
Cellulose	47.14 (± 0.86)
Hemicellulose	19.64 (± 0.11)
Lignin	22.11 (± 0.17)
Extractives (by difference)	6.63 (± 0.01)
^c Ash	0.46 (± 0.02)

commences. After each batch of approximately 100 kg, HCW is again recirculated to maintain process conditions. The feed barrel is reloaded with new premixed feed and processed continuously, and so on. Small amounts of CMC are added to the feed slurry (0.8 % on a mass basis) to prevent feed slurry sedimentation while processing a batch. In a single stage, the feed slurry is pressurized to process pressure (300 bar) by a high pressure piston pump. Hereafter the feed is heated in two serial heaters to process temperature (400 °C) with a heat ramp in the range of 200-400 °C/min. Two 5 L, heat-traced, serial reactors accommodate the reaction residence time. Reactor effluent phases are pre-cooled in a concentric-tube heat exchanger prior entering two parallel high-pressure filters. Depressurization and feed slurry mass flow is controlled by serial capillary tubes of various lengths and various diameters. Finally, the product phases are cooled to ambient conditions in a secondary cooler before separation.

2.4. Process conditions for liquefaction experiments

Process conditions were kept constant at 400 °C and 300 bar. Mass flow rate was approximately 9 kg/hr for Batch #1 and approximately 14 kg/hr for Batch #2, #3, and #4. During each batch run, mass balance samples were collected to evaluate process yields. In total, 14 mass balances were collected over the four batches.

2.5. Product separation procedure

Product phases (water phase and biocrude phase) were separated gravimetrically in a separation funnel. In contrast to small scale lab-experiments, using only a gravimetric separation procedure alleviates the need for expensive solvents and provides a more realistic

Table 2: Feed slurry composition of the four batches.

Feed composition						
Compound	Aspen wood	Glycerol	Water phase	K ₂ CO ₃	CMC	SUM
Mass fraction [%]	16.9	15.7	62.3	4.2	0.8	100

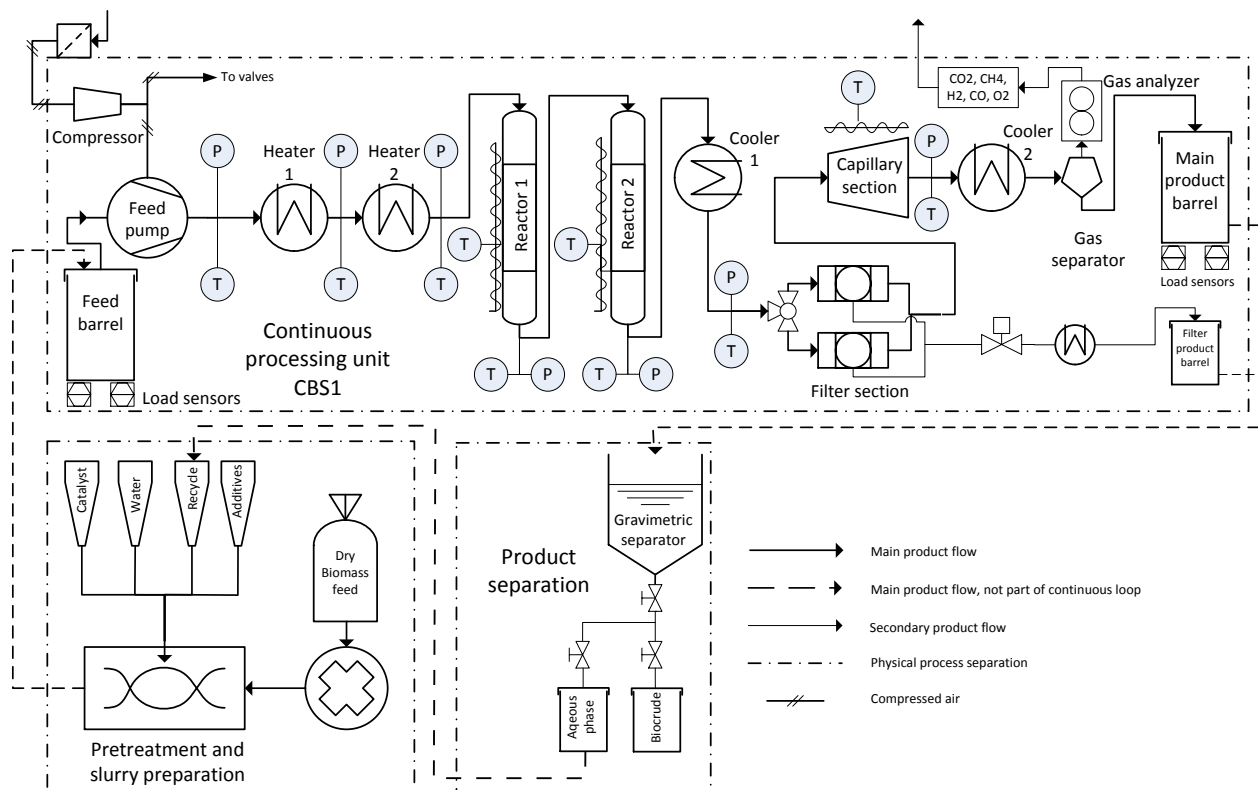


Figure 1: PFD of the CBS1 unit.

picture of economically viable yields. The biocrude and water phases were left to settle (30-60 minutes) before the water phase was tapped from the bottom of the funnel. Biocrude yields were measured right after the gravimetric separation. Product gases were collected and analyzed online for H_2 , CO_2 , CO , CH_4 , and O_2 .

2.6. Methods for biocrude and water phase analyses

Prior to biocrude analyses, the biocrude was centrifuged in a Sigma 6-16 HS centrifuge (2153 RCF) for 60 minutes to extract free water. Bound water was determined by Karl Fischer titration using a TitroLine 7500 KF. Elemental composition was measured using a Perkin Elmer 2400 Series II CHNS/O system (ASTM D5291). Calorific values were measured using an IKA C2000 oxygen combustion calorimeter (ASTM D2015). Qualitative analyses of all biocrude samples were carried out on a Thermo Scientific Trace 1300 ISQ GC-MS system, using a TG-SQC column (Length: 15 m., i.d.: 0.25 mm., film: 0.25 μ m film). Prior to analysis, all samples were diluted in diethyl ether (DEE) and subjected to the following oven temperature profile: 40 $^{\circ}C$ was held for 3 minutes, then ramped to 325 $^{\circ}C$ at 8 $^{\circ}C/min$ and finally kept at this temperature for 4 minutes. Injector and ion source temperatures were 280 $^{\circ}C$, split ratio was 1:20, and flow rate of the carrier gas (helium) was 1.0 mL/min. Compounds were identified by mass spectra comparison with the NIST mass spectral data library. Identification of all compounds by GC-MS is challenged by the complexity of the mixture and due to the fact only the volatile fraction is identifiable (roughly 50 % of the bulk biocrude). The identification of the reported compounds on the specific instrument was

confirmed by a round robin test. Total organic carbon (TOC) and potassium analyses of the water phases were performed on a Hach Lange Spectrophotometer with RFID.

Energy Recovery (ER), Carbon Recovery (CR), and the effective hydrogen-to-carbon ratio (H/C_{eff}) were calculated according to Eq. 1, 2, and 3:

$$ER = \frac{\text{HHV of biocrude} \cdot \text{mass of biocrude}}{\text{HHV of feedstock} \cdot \text{mass of feedstock}} \quad (1)$$

$$CR = \frac{\text{mass of C in the biocrude}}{\text{mass of C in the feedstock}} \quad (2)$$

$$H/C_{eff} = \frac{H - 2O}{C} \quad (3)$$

3. Results and Discussion

3.1. CBS1 performance

The performance and process stability in terms of process temperature, pressure, and mass flow rate of the CBS1 system is illustrated in Figure 2. The figure displays trend curves for a typical batch run, operating at a flow rate of approximately 14 kg/hr. It is readily observed that process conditions remains stable throughout the entire batch. Small pressure fluctuations in the beginning and in the end of a batch are observed, but these are explained by viscosity changes when feed is pumped into the system instead of HCW, and vice versa. The tiny oscillations in the pressure profile are due to the use of a piston pump.

For each mass balance sample roughly 20 kg of product (biocrude and water phase) was loaded into the funnel and left to separate gravimetrically before the water phase was tapped off at the bottom of the funnel. Figure 3 clearly shows a resulting hydrophobic supernatant biocrude. The yields of biocrude were based on this initial gravimetric separation, where bound water was not included. Furthermore, later centrifugal runs of the biocrude samples revealed yet unsettled water which naturally introduced unaccounted experimental errors on the biocrude yields. Figure 3 shows the yield calculations based on the mass balance samples obtained from the four batches. Due to significant yield variations within each batch, effects of water phase recirculation on the biocrude yields are somewhat inconclusive. As a result it is concluded that the separation procedure was not adequate for producing reliable yield results and a more robust and standardized separation procedure is under evaluation. Based on analysis of variations (ANOVA) calculations, it can only be concluded that yields from batch #3 are statistically higher than the yields from batch #4 (on a 95% confidence interval). During the liquefaction process water-soluble organics (WSO) are formed and contained in the aqueous phase. For batch #1, for which the feed slurry was prepared using demineralized water, it appears from Table 3 that the total organic carbon (TOC) content of the aqueous phase reaches a value of 54.1 g/L. after the first batch. Due to the recirculation procedure adopted, commenced after batch #1, it is observed that the TOC of the aqueous phase increases almost linearly to 136.2 g/L after the last batch. As the fraction of WSO in the aqueous phase increases, the biocrude and aqueous phase separation weakens since WSO act as co-solvents, leading ultimately to a single phase mixture, as it was found by Oasmaa et al. in a study on pyrolysis biooil separation [39]. As the amount of WSO increases, biocrude

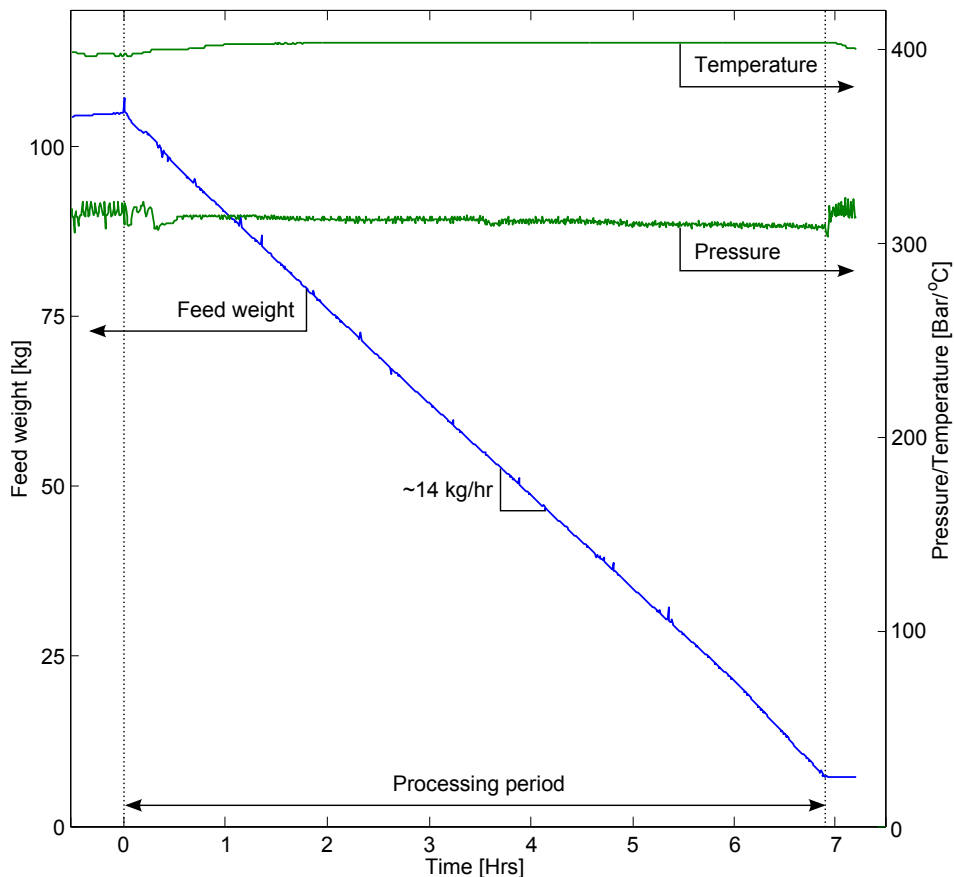


Figure 2: Process conditions, temperature, pressure, and feed barrel weight during a continuous batch run.

compounds become more soluble in the aqueous phase which could explain the tendency to a lower biocrude yield. The yield fluctuations also cause fluctuations in the energy (ER) and carbon recovery (CR) in the biocrude. In the present experiments, biocrude ER and CR ranges from 39-62 % and 42-66 %, respectively. Due to the fact that glycerol forms mostly WSO or gaseous products, the ER and CR are generally penalized when including the co-solvent fraction in the ER and CR calculations, which is only measured with respect to the biocrude.

Table 3 also shows that accompanying the accumulation of WSO in the aqueous phase, ash is likewise observed to accumulate as an equal amount of K_2CO_3 is added for each batch. Starting at an aqueous phase ash content of 6.2 %, resembling that of the original feed composition, the ash content is increasing linearly to a final value of 12.6 % after three recycles. Tracing the potassium in the water phase, it is observed that potassium accumulates linearly in the water phase. The mass fraction of potassium to the total water phase is almost half of the mass fraction of the TOC to the total water phase. It is also evident that after four batches (3 recycles) steady state values of the water phase has yet not been reached. During hydrothermal processing of glycerol, glycerol is mainly converted into WSO and hence the observation of WSO accumulation is likely to be a contribution from the high amount of glycerol added for each batch. Möller and Vogel investigated hydrothermal conversion of glycerol at 400 °C [16]. Even after 60 minutes, more than 10 % of the glycerol was

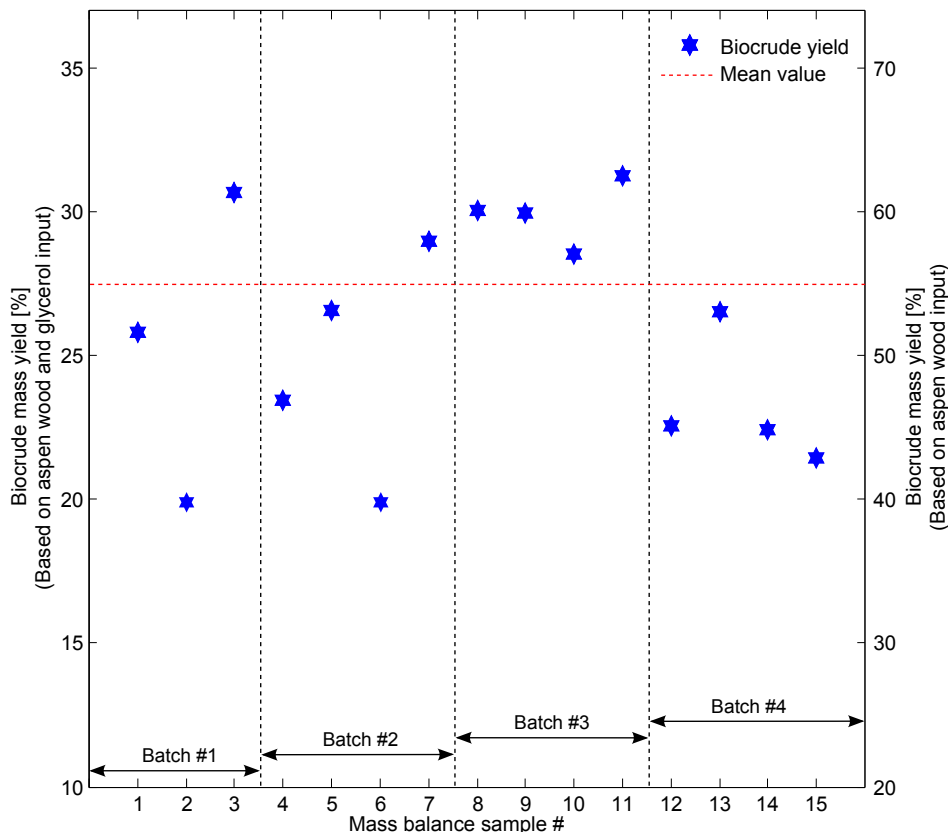


Figure 3: Biocrude yields obtained from mass balance samples during the four batches. Mean value of all the mass balance samples are presented. In the plot; display of a typical supernatant biocrude and water phase sample. The hydrophobic biocrude readily separates gravimetrically.

unconverted. During the present experiments, product analysis showed intact glycerol, but it was not clear how much glycerol was actually converted during processing. For continuous industrial operation with water phase recycling, ash accumulation presents an operational challenge to be addressed, as failing to do so may lead to operational malfunction. It has yet not been investigated, if the WSO containing water phase possess similar effects as glycerol on retardation of char formation. If so, glycerol may gradually be phased out as a feed additive as a work around for limiting the accumulation of WSO and still obtaining a stable process. The polarity of water as a solvent is known to diminish as it approaches near and supercritical water conditions, leading to solubility reduction for some salts, causing precipitation and ultimately plugging of the system. For the experiments reported here plugging was not experienced, nor did the campaign show signs of impending blockage, which would manifest itself as an increased pressure drop across the system.

Table 3 shows that after conversion the water phase is noticed to be acidic despite of the significant addition of alkaline catalyst. Lignocellulose and glycerol are known to form acidic compounds under hydrothermal processing, especially under alkaline conditions, which first neutralizes the K_2CO_3 , then later acidifies the water phase [16, 40]. Over the four batches the water phase pH appears almost invariant to the recirculation of aqueous phase.

To investigate if the aqueous recirculation affects the quality of the obtained biocrudes, an effective hydrogen-to-carbon ratio (H/C_{eff}) was calculated as a quality measure. Figure 4

Table 3: Aqueous phase analyses: Mass fraction of ash, total organic carbon (TOC), pH and potassium (K) content of the four different batches.

	Batch #1	Batch #2	Batch #3	Batch #4
Ash [%]	6.20	9.41	10.7	12.6
TOC [g/L]	54.1	96.9	106.3	136.2
pH	5.28	5.91	6.02	5.35
K [g/L]	27.2	50	56.4	61.7

shows the results. Like for the biocrude yields, some variations within the individual batches are noticed blurring a clear trend to be observed. However, when excluding Batch #1, it seems as the quality in terms of H/C_{eff} is increasing as water phase is recirculated. The improvement in biocrude quality by aqueous phase recycling has also been demonstrated by Elliott et al. [10]. A hypothesis is that WSO act as hydrogen-donors. By aqueous phase recirculation, the concentration of WSO increases, which in turn increases the concentration of hydrogen-donors.

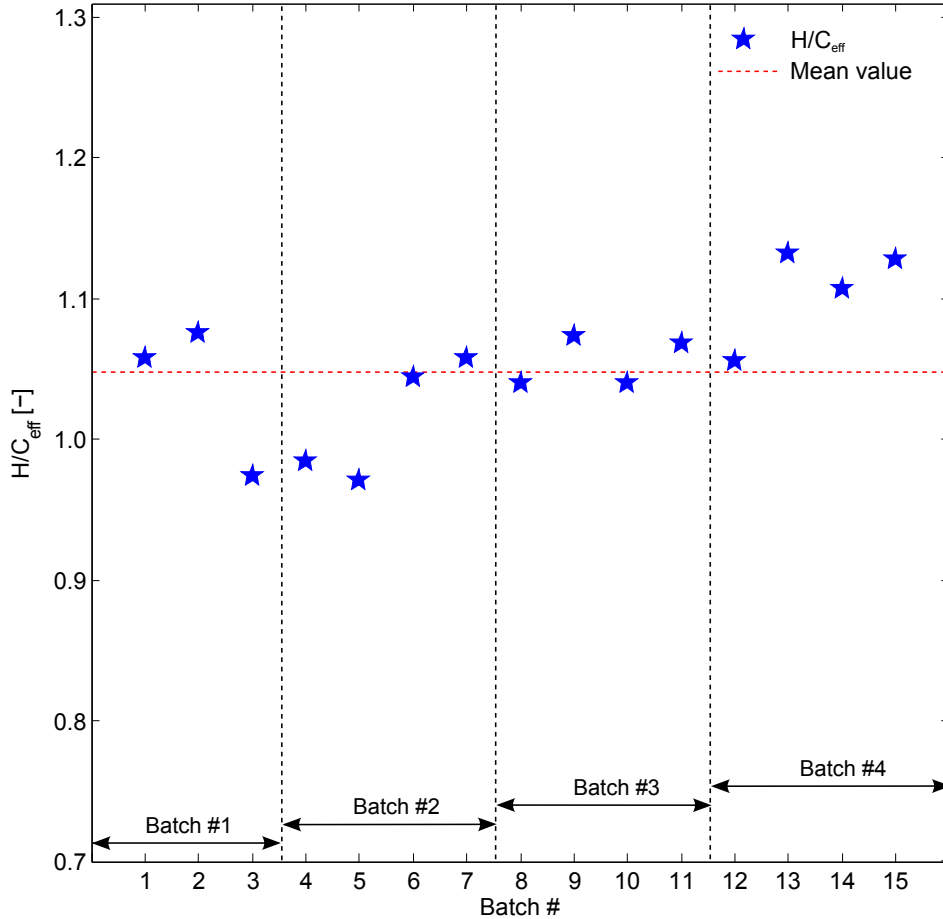


Figure 4: H/C_{eff} of the biocrude obtained from mass balance samples during the four batches. Mean value of all the mass balance samples are presented.

Gas phase composition was monitored continuously for carbon dioxide, hydrogen, methane, carbon monoxide, and oxygen throughout each batch. Figure 5 displays typical gas trends.

Initially, oxygen is diluted by producer gases and ultimately vanishes. It must be stated that the gas composition measured prior and in between batches is not precise, since gas detectors are calibrated only in a narrow band resembling process gas composition. It is noticed that the volume fractions CO_2 and H_2 reach steady state values of approximately 62 % and 30 %, respectively, and hence being the most abundant gases. The volume fractions of CH_4 and CO are 4-5 % and 2-3 %, respectively. During each mass balance samples, product gases are involuntarily exposed to surrounding conditions, allowing air to enter the gas stream. This is observed by an increased oxygen concentration, followed by decreasing product gases. After each mass balance sample steady state process conditions are reestablished as soon as the system is resealed. The gas mass flows were registered to approximately 0.6-0.7 kg/hr., amounting to a mass fraction of approximately 12-15 % of the input organic fraction. In terms of energy and carbon recoveries, this corresponds to approximately 2.4 % and 8.8 % in the gas phase. At best, the carbon balance across input and output phases was established at a 96 % closure.

Gas compositions obtained from the four batches are presented in Table 4, where the gas compositions have been normalized to exclude oxygen. It appears that the gas compositions are relatively invariant over the four runs and hence not affected by the water phase recirculation, although ashes and WS are observed to accumulate. The significant and insignificant shares of H_2 and CO , respectively, relative to uncatalyzed hydrothermal processing of lignocellulosic materials, indicate alternative chemical pathways [41–43]. Alkali catalysts have previously been found to enhance water-gas shift reactions, which can explain the high and low shares of H_2 and CO , respectively [44]. Steam reforming reactions may also be secondary contributors, but they proceed usually at much higher temperatures and in the presence of a transition metal catalyst [45]. A more speculative explanation is hydrogen abstraction reactions catalyzed by alkaline conditions. Glycerol deprotonation derives dihydroxyacetone, glyceraldehyde, and lactic acid, commonly observed WSO compounds, in addition to gaseous hydrogen [46].

Table 4: Normalized gas composition of CO_2 , CO , CH_4 , and H_2

	Gas phase volume fractions [%]			
	CO_2	CO	CH_4	H_2
Batch #1	62.1	2.9	4.6	30.5
Batch #2	62.1	2.9	4.6	30.5
Batch #3	60.8	2.7	4.5	32.0
Batch #4	63.6	3.3	4.2	28.8

3.2. Analyses of the biocrude

The biocrude was analyzed for determining the system performance in terms of biocrude quality. Table 5 compiles the bulk analysis obtained. First of all, it is observed that the mass fraction of oxygen in the biocrude (15.8 %) is significantly lower as compared to that of the feedstock (47 %, aspen wood plus glycerol). Secondly, the course of deoxygenation resulted in a hydrophobic, easily separable biocrude, with an increased gross calorific value (34.3 MJ/kg). The hydrophobicity of the biocrude is quantified by the low mass fraction of bound water in the biocrude (3.8 %). It is further observed that the ash content of the

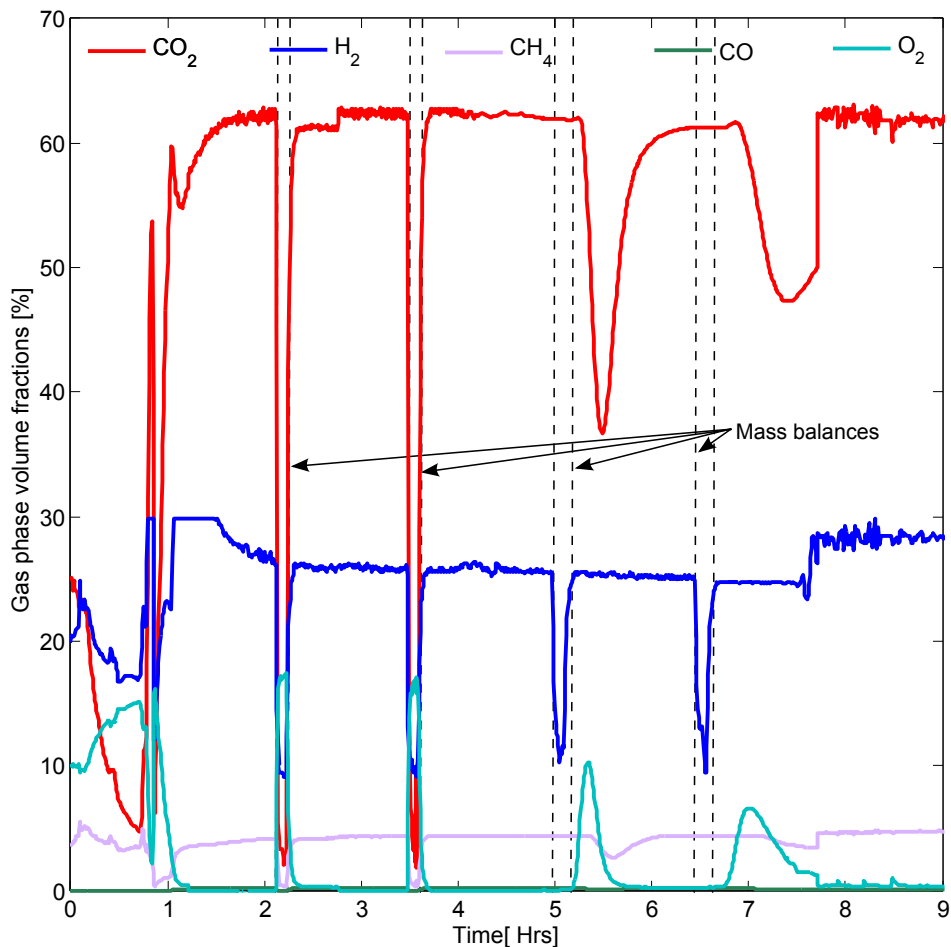


Figure 5: Continuous process gas composition. Initiations of mass balances are indicated in the figure.

biocrude is fairly high. The recycling effect of the ash content in the biocrude was not evaluated, but following the trends of the water phase, it is expected to increase from each aqueous phase recycle. A mass fraction of 0.48 % of undesirable inorganics poses a potential challenge, as inorganics mount a concern from a downstream point of view. A significant part of the inorganics is alkali metals, carried over by the high amount of K_2CO_3 added for each batch cycle. If the biocrude is to be refined, inorganics may decompose and deposit in refinery hardware or even poison expensive refining catalysts. If the biocrude is to be combusted directly, inorganics can cause corrosion, wear, and deposit in pumps, injectors, burners, turbines, *etc.* Hence, if the aqueous phase is to be recycled, procedure amendments have to be implemented. Accumulation of inorganics is of particular concern, which is why an inorganic removal step of the aqueous phase may have to be implemented downstream. A supercritical salt separator has previously been proposed as a means for precipitation various salts with high separation efficiency [47]. Furthermore, the accumulation of WSO in the aqueous phase must be investigated in greater details to understand, 1) the impact of WSO on the conversion mechanisms in terms of yields and product quality, and 2) the impact of WSO on the phase separation of the aqueous phase and the biocrude.

Table 5: Elemental mass analysis, higher heating value (HHV), mass fractions of ash and bound water of the biocrude, and biocrude ash composition.

Elemental analysis [% (daf)]		Metals [mg/g]	
C	75.2	Al	0.054
H	8.2	Cr	0.035
N	0.5	Fe	0.037
S	0.3	K	1.78
O	15.8	Mg	0.136
HHV [MJ/kg]	34.3	Zn	0.01
Ash content [%]	0.48	P	0.015
Bound water [%]	3.8	Ca	0.97
		S	0.1

The volatile fraction of the biocrude was further characterized to investigate the chemical composition. Table 6 presents the identified compounds by GC-MS analysis together with their chemical formulas, relative peak area, and number of carbon atoms (C#). It is readily observed that the biocrude is a complex mixture of chemical compounds for which the majority of compounds are oxygenated cyclic structures having carbon atoms in the range of C₆-C₂₁. Unsaturated hydrocarbons compounds with higher number of carbon atoms, including fused ring structures, were also identified but in minor quantities. The major denominators for all of the compounds are cyclic C₅ or aromatic C₆ backbones, substituted with various functional groups (ketonic, aldehyde, phenolic). Ketonic functionalities are mainly observed on pentane and pentene backbones having only single heteroatoms, and are believed to be formed by condensation reactions between Retro-Aldol derived carbohydrate intermediates. A broad collection of aromatics are also observed having mainly phenolic functionalities with single, double or even triple heteroatom formulas. Despite the fact that the compound mixture is complex and diverse, the range of numbers of carbon atoms is relatively narrow. The distribution of number of carbon atoms based on the identified compounds has been calculated semi-quantitatively by total ion count. The distribution is plotted in Figure 6, together with the common number of carbon atom ranges of conventional gasoline, kerosene-type jet fuel, and diesel. It appears that the majority of compounds lump into the C₆-C₁₂ region, mainly representing gasoline range and 'low cut' jet fuel. Based only on carbon range, the diesel range is hardly represented in the biocrude.

4. Conclusion

Continuous co-liquefaction of aspen wood and glycerol at supercritical water conditions was demonstrated successfully. High organic content feeds were prepared and processed for which a water phase recycling procedure was implemented. High process stability in terms of temperature, pressure, and mass flow rate was obtained and steady state conditions were achieved throughout all experiments. High hydrophobicity of the resulting biocrudes allowed for a simple, but commercially realistic, gravimetric separation between biocrudes and water phases. Unfortunately, significant yield variations obtained from mass balance samples within each batch obscured the identification of clear effects of the water phase recirculation on the

Table 6: List of compounds identified in the biocrude by gas chromatography-mass spectroscopy. The table includes compound name, formula, relative peak area, and number of carbon atoms (C#). No standards were used for compound verification.

RT (min)	Identified compound	Chemical Formula	Peak area (%)	C#
2.06	Cyclopentanone	C ₅ H ₈ O	0.30	5
2.59	3,5,5-trimethyl-2-hexene	C ₉ H ₁₈	0.39	9
2.94	2-methyl-cyclopentanone	C ₆ H ₁₀ O	2.28	6
3.37	ethylbenzene	C ₈ H ₁₀	0.39	8
3.56	p-xylene	C ₈ H ₁₀	0.62	8
3.87	2,5-dimethyl-cyclopentanone	C ₉ H ₁₆ O	0.86	9
4.04	3,4-dimethyl-3-penten-2-one	C ₇ H ₁₂ O	1.51	7
4.38	2-methyl-2-cyclopenten-1-one	C ₆ H ₈ O	1.58	6
5.04	1-cyclohexylethanol	C ₈ H ₁₆ O	2.84	7
5.19	1,2-dimethyl-cyclohexene	C ₈ H ₁₄	1.26	8
5.56	3-methyl-2-cyclopenten-1-one	C ₆ H ₈ O	1.83	6
6.93	2,3-dimethyl-2-cyclopenten-1-one	C ₇ H ₁₂ O	4.33	7
7.37	2,3,4-trimethyl-2-cyclopenten-1-one	C ₈ H ₁₂ O	4.32	8
7.65	p-cresol	C ₇ H ₈ O	1.75	7
8.12	2,3-dimethyl-phenol	C ₈ H ₁₀ O	2.71	8
8.50	2-ethylidenecyclohexanone	C ₈ H ₁₄ O	1.34	8
8.81	3,5-dimethyl-phenol	C ₈ H ₁₀ O	4.69	8
9.15	2,4,6-trimethyl-3-cyclohexen-1-carboxaldehyde	C ₁₀ H ₁₆ O	1.25	10
9.35	4-methyl-1-(1-methylethyl)-cyclohexene	C ₁₀ H ₁₈	1.32	10
9.44	4-methyl-1-(1-methylethyl)-cyclohexene	C ₁₀ H ₁₈	1.73	10
9.62	2,4,6-trimethyl-3-cyclohexen-1-carboxaldehyde	C ₁₀ H ₁₆ O	1.62	10
9.82	4-ethyl-3,4-dimethyl-2,5-cyclohexadien-1-one	C ₁₀ H ₁₄ O	1.31	10
10.14	2,4,6-trimethyl-3-cyclohexen-1-carboxaldehyde	C ₁₀ H ₁₆ O	1.50	10
10.71	2,6-dimethoxytoluene	C ₉ H ₁₂ O ₂	1.49	9
11.07	2,3-dihydroxy-3-methyl-1H-inden-1-one	C ₁₁ H ₁₂ O ₃	2.05	10
11.33	duroquinone	C ₁₀ H ₁₂ O ₂	0.86	11
11.71	2,6-dimethyl-1,4-benzenediol	C ₈ H ₁₀ O ₂	1.62	8
12.13	4-ethylcatechol	C ₈ H ₁₀ O ₂	1.92	8
12.42	2,5-dimethyl-1,4-benzenediol	C ₈ H ₁₀ O ₂	1.47	8
12.76	5-methoxy-2,3-dimethyl-phenol	C ₉ H ₁₂ O ₂	3.67	9
12.90	4-ethylguaiacol	C ₉ H ₁₂ O ₂	2.54	9
13.68	2,3,5-trimethyl-1,4-benzenediol	C ₉ H ₁₂ O ₂	4.21	9
13.97	3-tert-butyl-4-hydroxyanisole	C ₁₁ H ₁₆ O ₂	1.52	11
14.19	4-butoxybenzyl alcohol	C ₁₀ H ₁₆ O	0.93	10
14.81	2,3,5,6-tetramethyl-1,4-benzenediol	C ₁₀ H ₁₄ O ₂	1.52	10
15.30	2,6-dimethoxy-4-(2-propenyl)-phenol	C ₁₁ H ₁₄ O ₃	2.61	11
16.32	6-tert-butyl-2,4-dimethylphenol	C ₁₂ H ₁₈ O	1.20	12
16.44	Benzaldehyde, 3-hydroxy-4-methoxy-2-(2-propenyl)-	C ₁₁ H ₁₂ O ₃	0.81	12
16.63	4-(2,4,4-trimethyl-cyclohexa-1,5-dienyl)-but-3-en-2-one	C ₁₃ H ₁₈ O	0.64	13
18.82	methyl dehydroabietate	C ₂₁ H ₃₀ O ₂	0.36	21
19.79	10,18-bisnorabieta-5,7,9(10),11,13-pentene	C ₁₈ H ₂₂	0.74	18
20.82	retene	C ₁₈ H ₁₈	1.55	18

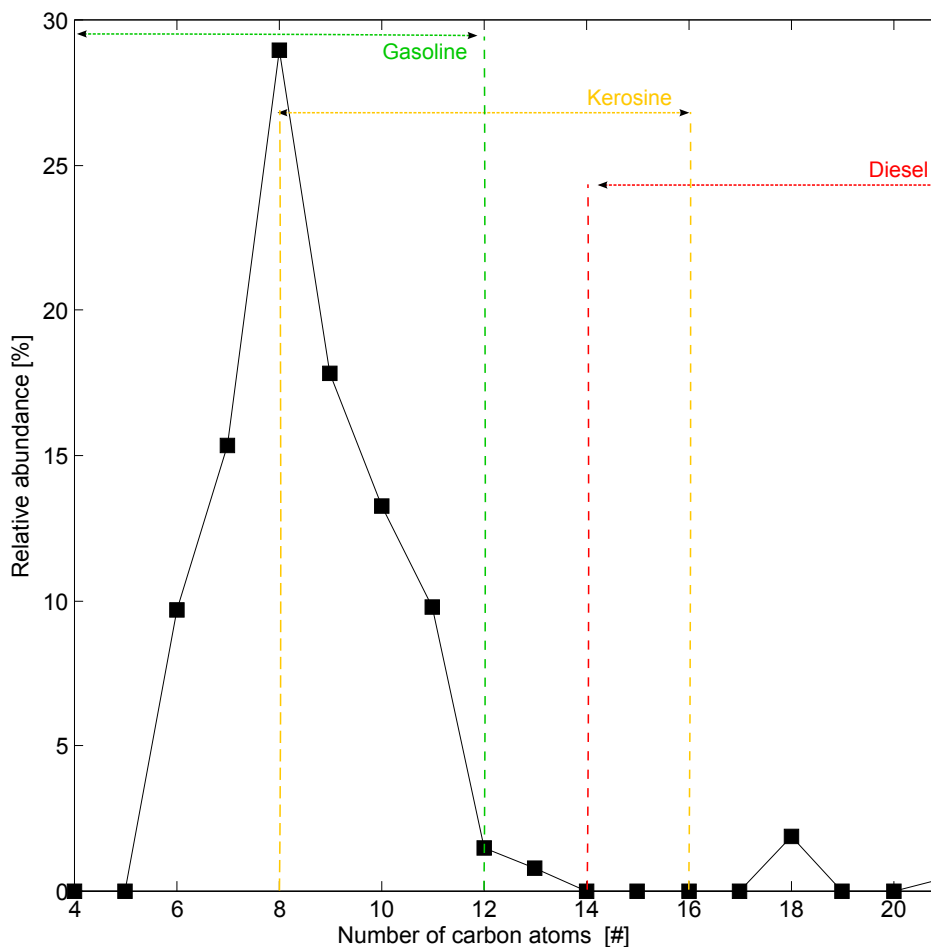


Figure 6: Relative distribution (by relative peak area) in numbers of carbon atoms in the compounds obtained from the identified in the biocrude. The relative abundance is calculated based on summed relative peak areas. The ranges of number of carbon atoms in conventional fuels are included.

biocrude yields, but a slight decreasing tendency is observed. Conversely the biocrude yield trend, the biocrude quality in terms of an effective hydrogen-to-carbon ratio was observed to increase slightly when the water phase is recirculated. Gas phase yields and compositions were found almost invariant to the water phase recirculation. Some process inconveniences were observed with respect to water phase recirculation; TOC and ash contents of the water phase were observed to increase significantly with water phase recirculation, which may eventually lead to system failure due to salt precipitation. Moreover, the mass fraction of ash in the biocrude was found relatively high (0.48 %). From the biocrude analysis it was found that the major biocrude compounds were cyclic C_5 or aromatic C_6 backbones, substituted with various oxygenated functionalities. The number of carbon atoms range of the biocrude compounds is distributed mainly in the C_6 - C_{12} range similar to gasoline. In conclusion, the experimental campaign demonstrated an auspicious platform for continuous operation of hydrothermal liquefaction for the production of high quality biocrudes.

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